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COMPLETE SPECIFICATION

NO DRAWINGS

Improving the Resistance to Soiling of Regenerated Cellulose

We, AMERICAN VISCOSE CORPORATION, of 1617 Pennsylvania Boulevard, Philadelphia, Pennsylvania, United States of America, a corporation organized and existing under the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to improving the resistance to soiling of regenerated cellulose fibres such as filaments and staple fibres of viscose rayon.

It has heretofore been suggested to coat cellulose fibres with deposits of finely divided silica to improve their slip resistance and their resistance to soiling. Also, various procedures have been suggested for the preparation of such silica coated fibres. For example, United States Patent No. 2,622,307 teaches the application of colloidal silica to the exposed pile portion of pile fabrics by spraying, brushing, etc., which results in a coating of the fibres which deteriorates substantially with successive cleaning treatments. Other examples of the prior art which disclose the application of colloidal silica have been exhaustively studied, but have failed to yield teachings which might be followed to obtain sufficient pick-up of silica particles by the fibres and adherence thereto to provide satisfactory soil resistance through a service period including a number of cleaning treatments. United States Patent No. 2,693,427, for instance, discloses the treatment of fibres in a bath containing a cationic surface-active agent and an inorganic salt, and then treatment in a dilute aqueous bath of colloidal silica. Although the cationic material is supposed to promote the deposition of silica on the fibre, and the

inorganic salt is present to aid in the deposition of the silica and to promote the fixation thereof, attempts to date to operate this two-bath process in a continuous manner have failed to give fibres loaded with sufficient permanently-fixed silica particles to effect soil resistance in accordance with standards desired in practising the present invention.

Specification No. 728237 describes a process for the treatment of textile fibres, yarns, and fabrics, and other textile materials by immersion in a colloidal solution of silica and then adding to the solution a water soluble metallic salt capable of producing in solution a positive ion having an ionic charge of at least three, so that silica is deposited from the colloidal solution on to the materials. Metallic salts specified are those of aluminium, iron and chromium.

It is a primary object of the present invention to provide silica-coated cellulose fibres and a method of producing them, such fibres being characterised by sufficient silica carried thereon to provide outstanding resistance to soiling, and by the improved adherence of the silica material to the fibres. Auxiliary to the foregoing object, it is a further object to provide a method for applying silica to cellulosic fibres in a simple one-step procedure. It is desired, moreover, that such procedure be applicable to the manufacturing of the fibres during an early stage thereof. A more specific object is to provide rayon fibres suitable for use in forming the pile of pile fabrics, such as carpets, plushes, and velvets, or the flock of flocked fabrics or other flocked products. These and other objects are obtained by treating the cellulose products with an aqueous colloidal suspension of grown silica particles or aggregates to which, prior to growth, has been added a small amount of a salt of a multivalent metal other than a

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basic metallic salt.

More particularly, the objects of this invention are obtained by treating regenerated cellulose with an aqueous suspension of silica containing a multivalent metal ion and in which at least 90% of the silica has an average particle size of about 0.5 to about 1.5 microns, preferably about 0.8 to 1.2 microns, removing excess aqueous suspension from the regenerated cellulose and thereafter drying the cellulose to fix the silica thereon, the aqueous silica suspension having been prepared by the addition of a hydrolyzable multivalent metal salt, other than a basic metal salt, to a silica sol of substantially smaller particle size following which the silica sol containing the hydrolyzable multivalent metal salt is aged in order to effect particle size growth to the particle size set out above. The presence of the multivalent metal ions also substantially improves the pick-up of silica by the cellulose and improves its adherence thereto. By this process, suspensions having the desired particle size can be prepared from silica sols of almost any smaller particle size including, though not restricted, to sizes of about 1 to 100 millimicrons. For the purpose of practicing the invention, however, the sols generally commercially available are used. These range in average particle size from about 12 to 20 millimicrons.

In preparing the colloidal silica treating solutions of the present invention, it is necessary after the multivalent metal salt has been added to the silica sol to permit the resulting composition to age until the formation of the larger particle size colloidal product has been obtained. It is interesting to note that though it may take from a few minutes to several hours, depending on the particular concentration and multivalent salt used, to complete the formation of the larger particle size silica, further growth to an average particle size much above about 1.5 microns does not occur to any appreciable extent. As a result, the treating suspension once formed may be permitted to stand for substantial periods of time. Though appreciable settling-out of the larger silica particle sizes or aggregates may occur on standing, this is apparently not detrimental and slight agitation is all that is needed to again disperse the silica particles or aggregates in the aqueous media.

Although the process of the present invention contemplates the use of any multivalent hydrolysable metal salt other than basic metal aluminium salts such as basic aluminium formate and basic aluminium chloride, it is generally preferred, particularly for the treatment of regenerated cellulose fibres for improvement in soil resistance, to use aluminium salts since aluminium imparts no color to the treated

fibres as would result from the use of other metals such as iron or copper. Examples of metal salts suitable for practicing the invention include aluminium formate, aluminium acetate, aluminium chloride, zinc chloride, zinc acetate, magnesium chloride, magnesium sulfate, ferric chloride, and cupric sulfate. Aluminium sulfate, including its double salts commonly referred to as alums, is generally preferred and will be used in the following more detailed description of the invention.

Colloidal silica products that are commercially available in quantity and are satisfactory for practicing the present invention include such products as "Ludox" (Registered Trade Mark) (made by E. I. du Pont de Nemours & Co.) and "Syton" (Registered Trade Mark) (made by Monsanto Chemical Co.). These products are procurable as concentrated dispersions of particle size under 50 millimicrons. Among the preferred silica sols used for practicing the present invention are the "Ludox" (Registered Trade Mark) colloidal aqueous sols containing about 30 percent colloidal silica of particle sizes in the range of about 15 to 20 millimicrons in diameter, about 0.30 percent sodium oxide and up to about 0.15 percent sodium sulfate. These sols have an approximate pH range of about 8.5 to 10.5.

It has been found, in investigations leading to the present invention, that the optimum average particle size of the silica aggregates for treating regenerated cellulose is approximately 1 micron in diameter, i.e., between 0.8 and 1.2 microns. An extremely uniform particle size is difficult to achieve, but dispersion in which the high preponderance of particles having sizes in the range named above and averaging closely to about 1 micron are readily obtainable in practicing this invention and are highly satisfactory. This average particle size value is desired because dispersions that may be employed for applying it to the fibres are more unstable if the average size is substantially larger than 1 micron, and the retention of the silica at larger particle sizes is somewhat lessened. The silica processing solutions preferred in this invention, however, are characterized by a slight instability, i.e., a tendency for the silica to settle out on standing. This minor amount of settling is not objectionable since the silica bath is normally agitated and the silica is maintained in suspension by the movement of fibrous material therethrough, and by the supplying and withdrawal of solution from the bath. Although it is recognized that the actual treating composition is not a true solution, but rather, a macro colloidal suspension of finely divided silica particles or aggregates in which appreciable settling may occur when

quiescent, for ease of describing the present invention it will be referred to as a treating solution.

From the foregoing, it is apparent that the manner in which the silica dispersion is prepared before contact with the fibres is an essential feature of the invention. An important step apparently not heretofore appreciated is that the silica solution, a sol, must be sufficiently aged after addition of the hydrolizable multivalent metal salt before application to the fibres in order to have particles of satisfactory uniformity and size within the treating bath before use. Though the aging period will vary somewhat with the particular multivalent metal salt added, for aluminium salts such as $\text{Al}_2(\text{SO}_4)_3$ and the alums satisfactory particle size and size distribution can be obtained with aging about 3 hours. However, greater uniformity of particle size may be obtained by longer aging, such as for a period of about 6 hours. Particle size may be controlled to some degree by the concentration of the ingredients mixed to form the silica bath for treating the fibres. The silica treating solutions when ready for use preferably have a silica content, based on the weight of the solution of about 0.05 to about 0.15 percent though treating solutions with silica content as high as 0.30 percent silica may be used. Where the aggregating salt is an aluminium salt, such as aluminium sulfate or alum, it should be used in amounts such that the aluminium is present in the treating solution, calculated on the basis of Al_2O_3 , in amounts of about 0.005 to 0.38 percent and preferably in amount of 0.0076 to 0.26 percent. Converting this to percent by weight of the salt, where the salt added is $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, which is the form in which aluminium sulfate is most readily available, the broad range would be about 0.03 to 0.25 by weight of the solution and the preferred range 0.05 percent to 0.15 percent. At the upper limits of the above broad ranges in the concentrations of either or both silica and aluminium sulfate, a suspension is formed that has a heavy colloidal appearance. If the concentration of aluminium sulfate is increased to, for example, 0.10 percent while using 0.05 percent of silica, an unstable dispersion is formed which results in a light precipitate. If larger percentages of silica are used with 0.10 percent of aluminium sulfate, still more unstable dispersions and heavier precipitates are formed. However, the precipitate is readily dispersed and its formation appears to have no detrimental effect. The pH of the silica bath at the recommended concentration of the ingredients lies within an approximate range of from about 4 to 5.

Although one of the effects of adding multivalent metal salts to commercial silica sols is to build up the particle size to a size

range that appears to be highly beneficial for treating cellulose products, the presence of multivalent metal ions such as aluminium also substantially improves the degree of silica exhaustion onto the cellulose and the adhesion of the silica to the cellulose. Treating cellulose fibres with aqueous silica suspension in which the silica has been reduced, for example by grinding, to a particle size of about one (1) micron will not give equivalent results even though the suspension has been acidified to a pH of 4 to 5. The presence of the multivalent metal ion is necessary to obtain the excellent adhesion between the silica and the cellulose obtained by the process of the present invention. This improved adhesion of the silica deposit and improved exhaustion of the silica onto the cellulose surface combine to give treated cellulose fibres having excellent soil resistant properties which are retained even after repeated washings.

For the best results, the fibres should be treated to render them soil-resistant while in the gel or so-called "green state". That is to say, they are thoroughly wetted with the silica solution at a stage in which they have attained a substantially regenerated state after spinning, but before they are dried to a point of equilibrium with atmospheric moisture. By treating in the "green state", a still further improvement in the retention of the silica by the cellulose is obtained. However, even though in preferred practice the regenerated cellulose is treated in the "green state", regenerated cellulose fibres which have been dried, may be rewetted and treated with solutions of the present invention and a substantial improvement in soil resistance obtained.

In applying the silica treating solution, the fibres are thoroughly wet with the treating solution for a period of about 2 to 30 minutes. A period of 2 minutes is sufficient for a continuous process although the period may be extended insofar as practical up to 30 minutes to insure the effectiveness of the deposition of silica. Longer periods, though not detrimental, serve no useful purpose. Thereafter, excess suspension is squeezed from the fibres such as by passing the fibres between a pair of nip rolls. The fibres may then be dried at any temperature up to about 107°C . Generally, higher drying temperatures should be avoided, particularly where the multivalent metal ion has been added in the form of a sulfate such as $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$.

In practice of the present invention an initial silica pick-up of about 1 percent by weight silica content of the fibres is regarded as generally preferred. At pick-up values of about 2 percent, some silica may tend to dust out of the fibres. This is generally objectionable, though for some purposes pick-up values as high as 3 percent silica

may be used. The lower limit of silica for effective improvement in non-soiling properties is about 0.3 percent. Lower amounts can of course be used but, for the prevention of soiling, are generally not sufficient to give wholly satisfactory results though some protection is obtained. When the fibre is dyed after the silica treatment a reduction in silica content of as much as 50 percent may result. However, this is a substantial improvement in silica retention over the prior art methods noted and still leaves the fibres with sufficient silica to substantially improve their resistance to soiling. The fibres which acquire silica in accordance with the teaching of this invention will normally require a lubricating-type finish for satisfactory processing in yarns and fabrics. The finish to be applied is preferably non-ionic. Examples of such finishes are sorbitol esters of palmitic and lauric acids, sorbitol monopalmitate, sorbitol monolaurate and sorbitan monooleate. These are used in the form of aqueous emulsions together with any suitable emulsifying agent such as polyoxyethylene modified sorbitan tristearate. Such finishes are conventionally applied in aqueous baths containing 0.1 to 2 percent of the finish material. Though the finish ingredients may be incorporated in the silica treating solution, it is preferred to use a separate bath for application of the finishing ingredients after the silica has been applied. This may be, and is preferably done prior to drying the fibres. In practice, it is generally

preferred to rinse the fibres after leaving the silica solution and the nip rolls so as to avoid dragging silica solution into the bath containing the finishing ingredients. Where the finishing ingredients are incorporated into the silica solution there is some tendency to inhibit silica pick-up of the fibres and to render the silica coating less fixed and more subject to loss through laundering.

The following examples will serve to further illustrate the invention:

EXAMPLE I

Fibre treating baths were made up by mixing aluminium sulfate and a concentrated solution of colloidal silica (average particle size 18 millimicrons) with a concentration of silica varying from 0.05 to 0.15 percent, and the aluminium sulfate (calculated on the basis of $Al_2(SO_4)_3 \cdot 18H_2O$) varying over a similar range of concentrations. The solutions were permitted to age for 3 hours for the development of particle size before application to the fibre. Separate staple masses were treated in each of the solutions. The typical treatment involved circulating the bath through the staple mass for a 10 minute period with the amount of the bath being at least 20 times greater than the amount of the fibre by weight. Table A specifies the concentration of silica and aluminium sulfate used with each sample, the appearance of the resulting silica bath, and the silica pick-up expressed as percent by weight silica of treated fibre.

TABLE A

Sample	Percent SiO_2	Percent $Al_2(SO_4)_3 \cdot 18H_2O$	Appearance	Silica Pick-up of SiO_2 in Fibre
1	.05	.05	Clear Colloid	0.71
2	.10	.05	Med. Colloid	1.10
3	.15	.05	Heavy Colloid	1.45
4	.05	.10	Very Light Prec.	0.73
5	.10	.10	Med. Precip.	0.87
6	.15	.10	Heavy Precip.	0.87
7	.05	.15	Heavy Precip.	0.52
8	.10	.15	Heavy Precip.	0.57
9	.15	.15	Heavy Precip.	0.75

Each sample of mass of fibre was centrifuged and dried at 107°C. Thereafter, a fatty acid ester of sorbitol finish was applied by circulating 0.15 percent solution through the staple. The staple was squeezed and dried the second time. All samples were dried and examined for silica pick-up, silica retention, and processability characteristics. After vigorous washing at 60°C, the fibres showed substantial retention of silica and good soil resistance. Sample 3 exhibited the best all-round properties with respect to soil resistance, silica retention and processability characteristics. The silica bath applied to Sample 3 was characterized by a fine dis-

persion which tended to settle out over a 24-hour period but was readily redispersed. This condition was found to coincide with and to indicate, as observed by microscopic counting, an average particle size of approximately 1 micron in which a very small fraction by weight of the particles had a size substantially less than about 0.5 micron or greater than about 1.5 micron. The finish staple, which was soft and processable, had by analysis 1.45 percent silica.

EXAMPLE II

A solution for applying silica to fibres was prepared by mixing aluminium sulfate, i.e., $Al_2(SO_4)_3 \cdot 18H_2O$, water, and a com-

mercially obtainable colloidal silica solution of which the silica had an average particle size of 18 millimicrons in such proportion as to provide a silica concentration of 0.05 percent and an aluminium sulfate concentration of 0.15 percent (calculated on the basis of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$). The solution was aged for at least three hours during which time the silica particles aggregated to form larger particles averaging in diameter about 0.9 of a micron. The sizes of the particles were determined by microscopic counting, and it was found that substantially more than half the particles by weight had a particle size greater than 0.8 micron and less than 1.2 microns. Less than 0.3 percent by weight of the particles was represented by sizes outside the range of 0.5 micron to 1.5 microns. Wet carpet fibre was admitted to a bath of the solution just described in a ratio of 1 part fibre to 25 parts of the bath. The treating temperature was 45°C. After the fibre had been immersed in the bath about 10 minutes, the fibres were squeezed, rinsed

in water, and dried at about 100°C. The fibres were analyzed for silica before and after dyeing with various direct dyes named immediately below.

Silica treated fibre	.76 percent silica	25
Silica treated fibres dyed with Chlorantine F		30
Brown BRL - Color Index No. P47	.35 percent silica	
Silica treated fibres dyed with Brilliant Benzo Blue 6BA - Color Index No. 518	.34 percent silica	35
In their dried state, the silica-treated fibres of this example showed no tendency to discharge dust.		40

EXAMPLE III

Fifteen denier bright crimped rayon fibres were treated according to the procedure described in Example II except that various samples of the fibres were treated separately with treating solutions made up in accordance with the concentrations indicated in Table B below:

TABLE B		
PERCENT SILICA IN SOLUTION	PERCENT ALUMINIUM SULFATE IN SOLUTION	PERCENT SILICA ON THE FIBRES
.05	.05	.81
.15	.05	1.63
.05	.10	.75
.15	.10	1.16
.05	.15	.59
.15	.15	.91

From the data provided in Table B, it will be observed that the greatest deposition was obtained in the fibre samples treated with solutions in which the aluminium sulfate content was low relative to the silica content.

EXAMPLE IV

A silica treating solution was prepared at a silica concentration of .15 percent and an aluminium sulfate concentration of 0.10 percent. The solution was aged 3 hours to obtain a particle size of approximately 1 micron and then applied to 15 denier dull crimped viscose staple by showering the solution over the fibres while carried on a conveyor. A sample of the solution showed a tendency of the silica aggregations to settle over a 24-hour period. The application of the solution to the fibres was made at 45°C. and was continued for 10 minutes. The staple fibres were centrifuged and dried at 100°C. Thereafter, the fibres were treated with a lubricating finish comprising a sorbitol fatty acid ester for making the fibres more processable.

The staple fibres were formed into yarn which in turn was made into tufted carpet samples. A carpet sample was dyed in a dye beck in a conventional manner. Analysis of the carpet fibre for silica was made before and after dyeing. The silica values of the

carpet were as follows:

After opening (by cotton processing)	1.13 percent	
After tufting (carpet sample)	1.10 percent	90
After dyeing (carpet sample)	0.40 percent	
Samples of carpets comprising silica-treated undyed fibres, silica-treated dyed fibres, and untreated fibres were subjected to a service floor test. Substantial improvement in soil resistance over the carpet sample of untreated fibres was observed in the carpet samples made of silica-treated fibres. The undyed sample having the greater silica content was found to be the least soiled.		100

EXAMPLE V

A solution for treating fibres was prepared having a concentration of 0.10 percent of silica and 0.05 percent of alum ($\text{Al}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$). The solution was aged 5 hours and then applied in the form of a shower to a blanket of viscose staple fibres continuously for a period of 5 minutes. Staple fibres were centrifuged and dried at 80°C. The fibres were found to have gained 0.9 percent in weight as the result of silica pick-up. The fibres were thereafter washed and dried to ascertain the ability thereof to retain silica. On being reweighed, the silica content was found to be about 0.75 percent. The fibres were tested in the laboratory

along with a control sample for soil retention and found to retain substantially less of the soiling material than the control sample. The silica solution prepared in accordance with this example showed a tendency to settle on standing for a 24-hour period, but the silica was readily resuspended by slight agitation of the suspension.

EXAMPLE VI

10 A solution having a concentration of 0.15 percent silica and 0.20 percent $\text{Al}(\text{C}_2\text{H}_5\text{O}_2)_3$, equivalent to 0.10 percent Al_2O_3 , was prepared for treating fibres. The solution was aged for 3 hours after which rayon carpet fibres were
15 immersed in the solution for 10 minutes at 45°C ., agitating the fibres during the treatment. The fibres were squeezed to a weight equivalent to 200 percent of their dry weight, rinsed in water, centrifuged and dried at
20 100°C .. Analysis of the fibres showed a pick-up of 0.85 percent SiO_2 . Application of a sorbitol fatty acid ester finish in a concentration of 0.1 percent softened the fibres sufficiently to permit processing without
25 dusting of the SiO_2 or fibre breakdown.

The foregoing examples illustrate the essential features of the invention as well as some of the manners in which the invention may be practiced. They show how silica
30 in sufficient quantities to prevent soil resistance may be applied to fibres by first preparing a suspension of the silica comprising the disclosed ingredients in the desired proportions, and properly aging the
35 solution before use in order to have the desired particle size. In this manner, the silica may be deposited on the fibres in the required amounts and in a manner such as to improve its adherence while using a single
40 bath, thus avoiding the effort expended in carrying out the more complicated procedures of the prior art. It is believed that the character of the cation of the hydrolyzable salt used for aggregating the silica
45 particles, the proportions of the ingredients, and adequate aging are all important with respect to obtaining efficient silica pickup and the retention thereof by the fibres.

WHAT WE CLAIM IS:—

50 1. Method of improving the soil resistance of regenerated cellulose, characterized by treating the regenerated cellulose with an aqueous suspension of silica containing a multivalent metal ion and in which
55 at least 90% of the silica has an average particle size of about 0.5 to about 1.5

microns, preferably about 0.8 to 1.2 microns, removing excess aqueous suspension from the regenerated cellulose and thereafter drying the cellulose to adhere the silica thereon, the aqueous silica suspension having been prepared through addition of a hydrolyzable multivalent metal salt, other than a basic metal salt, to a silica sol of substantially smaller particle size, followed by aging. 65

2. Method according to claim 1, characterized in that the aqueous suspension contains about 0.05 to 0.30%, preferably no more than 0.15%, silica.

3. Method according to claim 1 or 2, characterized in that said multivalent metal ion is aluminium, the metal salt being, for instance, aluminium sulfate. 70

4. Method according to claim 3, characterized in that sufficient aluminium salt is added to the silica sol to give a calculated Al_2O_3 content of about 0.005 to 0.38% by weight, preferably about 0.0076 to 0.26%. 75

5. Method according to any of the preceding claims, characterized in that the aqueous suspension has been aged for at least three hours prior to treating the regenerated cellulose. 80

6. Method according to any of the preceding claims, characterized in that the regenerated cellulose is treated prior to drying after being formed. 85

7. Method according to any of the preceding claims, characterized in that the treated regenerated cellulose is further treated with an aqueous bath containing a lubricating-type finish after excess aqueous suspension is removed and before drying. 90

8. A composition for treating regenerated cellulose, characterized in that it contains the aqueous suspension obtained according to the method claimed in claims 1 to 5. 95

9. The method of improving the soil resistance of regenerated cellulose substantially as hereinbefore described. 100

10. The improved composition for treating regenerated cellulose substantially as hereinbefore described.

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